OPTICAL GAIN IN Er-DOPED LARGE-BANDGAP SEMICONDUCTORS GaN AND ZnO

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14. ABSTRACT

Infrared emission from Er3+ ions embedded in GaN and in non-conventional Si-based nanomedia has been investigated in order to develop fundamental understanding of physical processes governing its efficiency. In particular, excitation mechanisms have been examined. For the GaN:Er, where direct and host-mediated excitations are possible, detailed information on the multiplicity and the excitation mechanism of optical centers has been obtained by combining information from emission and excitation spectroscopy. For Er-doped heterogeneous medium of Si-nanocrystals dispersed in SiO2, details of sensitization process were examined. We have shown, that the enhancement of excitation cross-section concerns only a very small percentage of Er dopants and has internal limits imposed by finite time duration of energy transfer processes. We conclude that optical gain is unlikely to be achieved in this system. For Si/Si:Er multinanolayer structures, in which preferential formation of a single type of high-symmetry Er center is realized, we have shown that creation of excitons is not strictly necessary for Er excitation. Further, we have identified a new excitation channel with photon energies close to Si bandgap. Since efficiency of this ¡§resonant¡¨ process exceeds that of the band-to-band pumping, it opens new prospects for optical activation of Si:Er. We have also investigated the 2.7£gm emission from Er. For Si, we have theoretically modeled a possible excitation path and tested it experimentally. For GaN, we have looked for evidence of the 4I11/2 _ 4I13/2 transition both in emission at Ü = 2.7 £gm, and in the rise time of the 1.5 £gm band. Since no conclusive results were obtained, we scrutinized in detail radiative and non-radiative recombinations for Er3+ ions in a truly insulating host. We have explicitly shown that in this case both lowest excited states (4I11/2 and 4I13/2) are characterized by long radiative lifetimes, offering a possibility to develop population inversion.

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Abstract

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For Er-doped heterogeneous medium of Si-nanocrystals dispersed in SiO_2, details of sensitization process were examined. We have shown, that the enhancement of excitation cross-section concerns only a very small percentage of Er dopants and has internal limits imposed by finite time duration of energy transfer processes. We conclude that optical gain is unlikely to be achieved in this system.

For Si/Si:Er multinanolayer structures, in which preferential formation of a single type of high-symmetry Er center is realized, we have shown that creation of excitons is not strictly necessary for Er excitation. Further, we have identified a new excitation channel with photon energies close to Si bandgap. Since efficiency of this "resonant" process exceeds that of the band-to-band pumping, it opens new prospects for optical activation of Si:Er.

We have also investigated the 2.7μm emission from Er. For Si, we have theoretically modeled a possible excitation path and tested it experimentally. For GaN, we have looked for evidence of the $^4I_{11/2} \to {}^4I_{13/2}$ transition both in emission at $\lambda = 2.7$ μm, and in the rise time of the 1.5 μm band. Since no conclusive results were obtained, we scrutinized in detail radiative and non-radiative recombinations for Er^{3+} ions in a truly insulating host. We have explicitly shown that in this case both lowest excited states ($^4I_{11/2}$ and $^4I_{13/2}$) are characterized by long radiative lifetimes, offering a possibility to develop population inversion.

Key words

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List of participating scientific personnel

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1. INTRODUCTION

Rare Earth (RE) ions are frequently used as optical dopants to improve radiative recombination of (indirect) semiconductors, or/and to tailor these recombinations to a wavelength of choice. From a variety of explored dopants, Er attracts particular attention, since its characteristic emission at $\lambda \approx 1.5$ µm coincides with the absorption minimum of glass fibers commonly used in nowadays communication networks. The somewhat less explored $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition at $\lambda = 2.7$ µm between the second and the first excited states offers a possibility to realize an emitter in the wavelength interesting for sensing, telecommunication, and also surgical applications. In this report we present results of the project, where we explored processes of optical excitation and recombination related to Er^{3+} ions embedded in selected semiconducting media of practical importance for device development: MBE-grown GaN layers, dispersions of Si nanocrystallites in SiO_2, and recently developed unique structures containing multiple stacks on Si:Er nanolayers separated by spacer layers of undoped Si. (For Er-implanted ZnO, whose investigation has also been scheduled in the project, no Er-related emission has been observed, in spite of different thermal treatments). The experimental approach is steady-state and time-resolved excitation, emission, and two color spectroscopy using a variety of continuous-wave and pulsed laser sources covering a broad range of far- (80 µm), and mid- (4 – 20 µm) infrared, as well as near-infrared and the visible (2.4 µm – 320 nm).

In what follows a brief description of the main results obtained for each of the above-mentioned specific research subjects is presented, followed by a list of relevant publications prepared within the project period.

2. IR Er-RELATED EMISSION FROM MBE-GROWN GaN:Er LAYERS

In spite of the impressive progress of GaN technology in recent years, its quality remains inferior when compared to the "mainstream" electronic materials for device manufacturing as Si and GaAs. In particular, deep mid-gap states present a problem. This has been directly illustrated by results of two-color spectroscopy on epitaxially grown GaN layers, obtained in the framework of this project. We have compared photoluminescence induced under band-to-band excitation with and without additional infrared illumination of tunable wavelength. We have observed that the intensity of the donor-related emission was strongly affected by the infrared radiation. From characteristics of the effect, we have concluded that deep mid-gap states were involved in the investigated emission channel.

Following this initial step, we have moved to investigate the MBE-grown layers of Er-doped GaN. These were obtained from Dr. A. Steckl, University of Cincinnati. Our studies were focused on the 1.5 µm emission band. In particular, we addressed two important issues:

    A. Multiplicity of Er-related optical centers formed in these materials.
    B. (The possibility of) population of the $^4I_{13/2}$ excited state of the Er^{3+} ion by a (slow) radiative process.

Ad. A: The existing reports on the Er-doped MBE-grown GaN layers conclude [1,2] that different types of Er-related centers coexist in these materials and simultaneously contribute to the 1.5 µm emission band. The individual centers can be distinguished by excitation mode as different spectra are obtained upon band-to-band and resonant

excitation mode (at room temperature). These findings are not confirmed in the present project, which might indicate that preferential formation of a particular type of Er-related center might have been realized in the investigated materials.
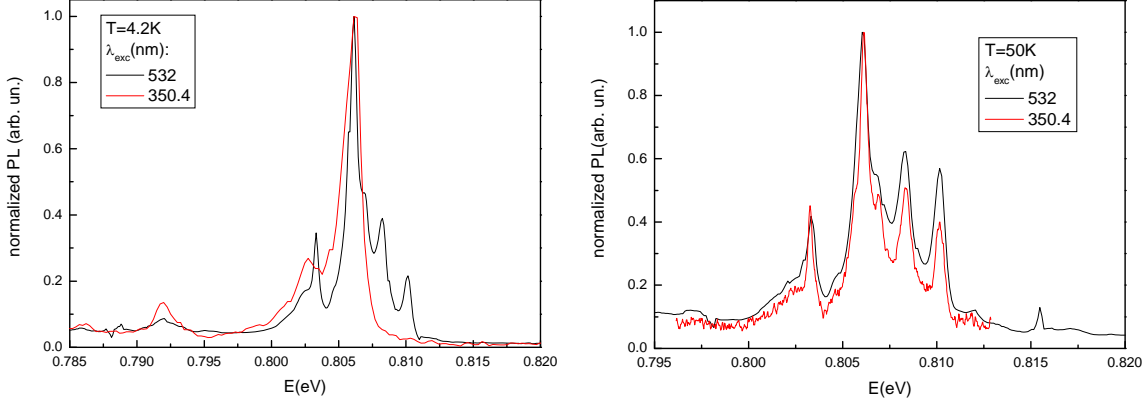

Fig.1: *High-resolution spectra of the 1.5μm Er-related PL band as measured under resonant (532 nm) and band-to-band (350 nm) excitation at 4.2 and 50 K*

Fig.1 shows the 1.5 μm PL band as measured under direct (resonant) and indirect (via the host) excitation. As can be seen, for T=50K (and also at higher temperatures) a truly identical spectrum is obtained regardless of the excitation mode. Some differences appear only in the spectra taken at the lowest temperature of the sample – left panel, where some peaks at the higher energy side, are not visible upon band-to-band pumping. In our opinion, however, these lines do not belong to a different center but, most probably, represent transitions from upper crystal-field split sublevels of the excited state ("hot lines"), which appear at higher pumping rates. Therefore, while generation of a variety of Er-related optical centers cannot be ruled out in view of the relatively large bandwidth of 1-3 meV, we do not find any evidence that distinction between them can be made by the excitation mode. Alternatively, such a behavior could indicate a very efficient excitation transfer between microscopically different centers, as these two possibilities are very difficult to separate experimentally. The energy exchange should increase with temperature, which would then provide also an alternative interpretation of the spectral differences appearing in the 1.5 μm band at the lowest temperature. For completeness, we point out that the existing reports assigned individual well-resolved peaks of this band to microscopically different centers ("sites") – all of them, however appearing upon band-to-band excitation, which is at variance with our findings [2].

Also careful investigation of the excitation spectrum of the 1.5 μm IR band did not bring evidence for multiplicity of Er-related centers. Although we have found at room temperature a sizeable two-fold splitting of the major (excitation) lines corresponding to the $^4I_{15/2} \rightarrow {}^2H_{11/2}$ (~ 2.33 eV), $^4I_{15/2} \rightarrow {}^4I_{9/2}$ (~ 1.5 eV), and $^4I_{15/2} \rightarrow {}^4I_{11/2}$ (~ 1.26 eV) transitions, identical PL spectra of the 1.5 μm band were obtained at every component of the excitation bands. Moreover, the intensity of separate components was temperature dependent, and, while the actual splitting is different for the two bands, a similar
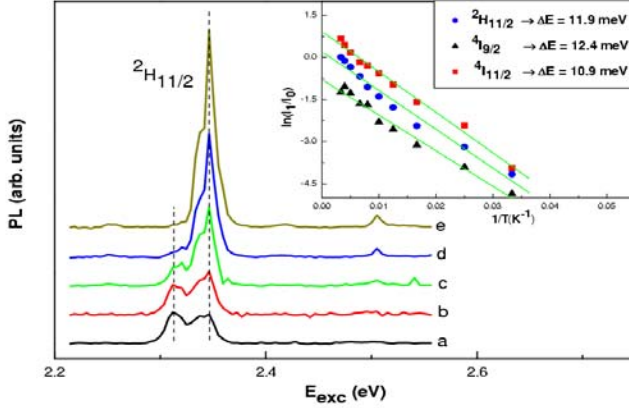
Fig.2: *Low-temperature (LHe) PLE spectra for the* $^4I_{15/2} \to {}^2I_{11/2}$ *transition as recorded for the most pronounced peak of the 1.5 μm Er-related PL band. The inset shows that thermalization of two proceeds in a similar manner for all the major excitation bands.*

activation energy of ~ 11-12 meV is derived from the Arrhenius plot of the intensity ratio the two components. This is illustrated in Fig.2 for the $^4I_{15/2} \to {}^2H_{11/2}$ transition within the 4f-electron shell of an Er^{3+} ion. We conclude that the observed splitting of the excitation lines arises due to thermalization within the ground multiplet of the same center, with the individual transitions taking place to different levels in the upper-lying states. Again, for the sake of completeness, we note that the existing reports [2] indicate fine structure of the excitation bands (observed for "green" and "red" emission), not resolved in our study, but do not show the large splitting appearing for all the bands, as revealed here.

Ad. B: According to available studies [1], an Er^{3+} ion at a high-symmetry substitutional Ga site might be a plausible candidate for realization the 2.7 μm emission. Exploration of this was among the goals of the project. Such a possibility followed from an observation that the kinetics of the 1.5 μm band related to that center shows a slow (~ 1 ms) rise time. Since the $^4I_{13/2}$ level responsible for this emission is populated by the $^4I_{11/2} \to {}^4I_{13/2}$ transition, this slow increase of PL signal is indicative of radiative character of this transition.

Indeed, such a possibility can be anticipated for GaN:Er, as radiative recombination tends to dominate transitions between levels separated by more than 5-6 lattice phonons. This condition is fulfilled for the $^4I_{11/2} \to {}^4I_{13/2}$ transition of Er^{3+} ion in GaN: $\Delta E = 0.46$ eV, $E_{LO\text{-}ph} = 68$ meV. Moreover, rare-earth ions are usually very weakly coupled to the lattice, due to the effective shielding of the 4f-electron shell responsible for excitations. In contrast to that, in the present study we did not find any slow-rising component within the 1.5 μm band. Regardless of the particular transition used for resonant excitation, the rise time determined by temporal resolution of our system has been observed. In addition, in the low-temperature PL spectra, we have identified replicas on both high- and low-energy side of the 1.5 μm band. Since careful analysis revealed that these are equally spaced, the observed replicas are not likely to correspond to transitions from different levels of the (crystal field split) excited state; rather they arise due to (local) phonons participating in radiative recombination. We note also that an observation of lattice phonon replicas has recently been reported for the "green" emission from GaN:Er [2]. Taken together, these results cast severe doubts whether a radiative $^4I_{11/2} \to {}^4I_{13/2}$ transition can be realized for Er^{3+} ions embedded in GaN. In view of that, we extended our investigation to a truly insulating Er-doped host – see the last section of the report.

Papers referred to:

1. F. Pellé *et al.* Mater. Sci. Eng. B **105**, 126 (2003)
2. V. Dierolf *et al.* J. Appl. Phys. **95**, 5464 (2004)

Relevant papers prepared within the project period
   Other journals
   1. M. Wojdak, M.A.J. Klik, M. Forcales, T. Gregorkiewicz, J-P.R. Wells, K. Pakuła, J.M. Baranowski, S. Porowski, *"Photoluminescence of GaN layers studied with two-color spectroscopy"*, Sol. St. Electronics **47**, 579-581 (2003).
   2. I. Izeddin, T. Gregorkiewicz, A.J. Steckl, and D.S. Lee: *"Time-resolved photoluminescence and excitation spectroscopy of the 1.5μm Er-related band in MBE-grown GaN layers"*, to appear in Superlattices and Microsctructures (2004).

3. SENSITIZATION LIMITS OF SiO_2:Er BY Si NANOCRYSTALS

Dispersions of Si-nanocrystals (nc's) in Er-doped SiO_2 matrix has recently been vividly debated as an Er-doped medium fully compatible with the Si platform, in which intense room-temperature 1.5 μm emission, and poss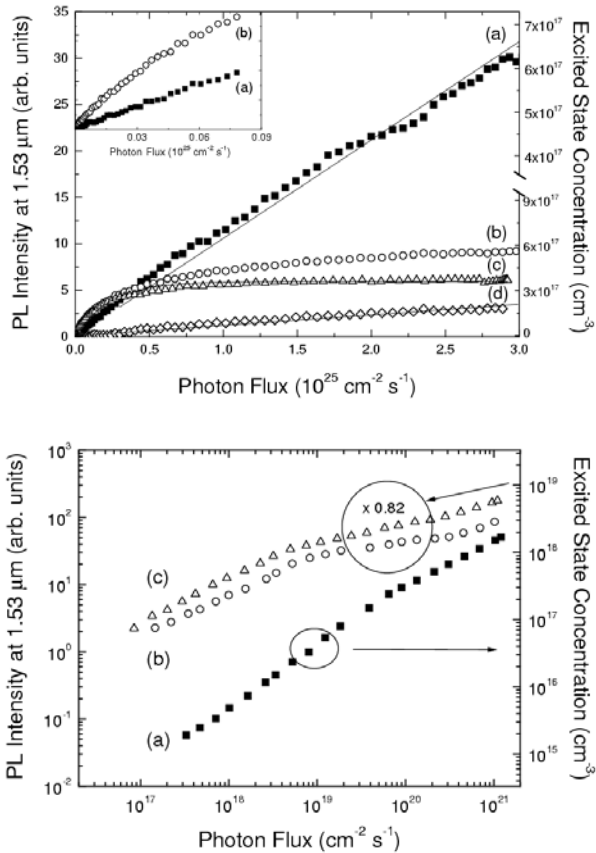ibly also optical amplification, could be realized. In order to evaluate this, we have undertaken a comprehensive investigation of this medium using resonant and nonresonant, pulsed and continuous wave (cw) pumping at variable wavelength (in collaboration with F. Priolo, Univ. of Catania, Italy). In Fig.3, we summarize the major result of this research: we show PL intensity as function of photon flux for a SiO_2:Er sample sensitized with Si nanocrystals under resonant (○) and nonresonant (*A*) pulsed and cw excitation. On the right-hand vertical axis the concentration of Er atoms in the excited state is given. It is derived from respective results obtained for an unsensitized SiO_2:Er sample (■). In the inset to the top panel, a detailed dependence for small photon flux is depicted. From the results presented in Fig.3 we conclude that only a small fraction of the total concentration (2.2×10^{20} cm^{-3}) of the available Er^{3+} ions – ~0.15% for pulsed and ~3% for cw pumping – can be excited in the efficient process mediated by Si nc's. Moreover, the concentration of

Fig.3: *Photon flux dependence of 1.5 μm emission from SiO_2:Er(■) and SiO_2:Er,Si-nc under resonant (○) and nonresonant (A) pulsed (top panel) and cw (bottom panel) excitation*

optically active Er centers is significantly reduced upon introduction of Si-nc's – more than 50% of Er^{3+} ions cannot be excited at all, either indirectly or directly.

We conclude that although sensitization by Si nc's allows for an efficient non-resonant excitation of Er^{3+} ions in SiO_2, population inversion will require detailed engineering, and thus is not likely in samples prepared by self organization.

Relevant papers prepared within the project period
APS journals
1. M. Wojdak, M. Klik, M. Forcales, O.B. Gusev, T. Gregorkiewicz, D. Pacifici, G. Franzò, F. Priolo, F. Iacona, *"Sensitization of Er luminescence by Si nanoclusters"*, Phys. Rev. B **69** 233315:1-4 (2004). (also selected by Editors for publication in the July 14, 2004 issue of Virtual Journal of Nanoscale Science & Technology)
Other journals
1. M. Forcales, M. Wojdak, M.A.J. Klik, T. Gregorkiewicz, O.B. Gusev, G. Franzò, D. Pacifici, F. Priolo, and F. Iacona, *"Si nanocrystals as sensitizers for Er PL in SiO₂"*, MRS Symposia Proceedings Vol. **770**, pp. 119-124, edited by Tom Gregorkiewicz, Robert G. Elliman, Philippe M. Fauchet, James A. Hutchby, Materials Research Society, Warrendale, Pennsylvania (2003).

4. SPECIFIC ASPECTS OF EXCITATION PROCESS IN Si:Er NANOLAYERS

After a period of initial enthusiasm, investigations of Si:Er stagnated, as hopes for development of practical telecommunication devices based on this system faded away. This is due to the fact that in spite of research effort by many different groups, efficient and temperature-stable 1.5 μm emission from this system was not demonstrated. It has become clear that the problems limiting emission from Si:Er are of fundamental nature, and could not be solved by materials engineering alone.

Si/Si:Er multinanolayer structures offer opportunities to overcome the limitations of Si:Er, and in that way open new hopes for optical amplification in Si. The group of PI has been involved in this research from the very beginning and provided major contributions proving practical importance of the nanolayered structures. In particular, we have demonstrated that preferential formation of a single type of Er-related optical center was possible in these structures. Until now this was not possible, as Er implantation, commonly used for preparation of Si:Er materials, results in formation of a multiplicity of centers. Preferential generation of a single Er-related optically active center is a major step toward Si photonics based on Er doping, and has always been seen as a necessary prerequisite for development of a Si:Er-based laser. Moreover, the ultra small bandwidth of the Er-related emission from Si/Si:Er nanolayers has dramatic consequences for the expected gain coefficient. We conclude that these structures offer a possibility to increase the excitation cross section by as much as factor 10^3 when compared Si:Er materials prepared by ion implantation. The resulting gain coefficient should improve even more, as we have also shown that a higher percentage of optically active Er species can be achieved in the nanolayer structures than in implanted samples.

On the more fundamental side, we note that the nanolayer structures offer ideal conditions for investigation of details of the excitation process of Er in a Si matrix, which is still not fully understood. Since absorption and emission regions are spatially separated (absorption of incoming photons, and efficient exciton generation, takes place in *spacer* layers of pure silicon, while emission is realized in Er-rich *active* regions), exciton-mediated energy transfer is significantly promoted and can be conveniently separated from other excitation mechanisms. On the other hand, the Auger process of Er excitation quenching by free carriers is suppressed. Taking advantage of this situation, we have investigated Er PL in a nanolayer structure under pulsed pumping at variable wavelength. In that way we have analyzed and successfully modeled the Er excitation process by an electron-hole plasma and shown that localization of an exciton at an Er-related level is

not a necessary step in the PL mechanism (as assumed in all the models existing at present). We have also identified a new excitation process of resonant character. This is illustrated in Fig.4, where the excitation dependence of the 1.5 µm Er-related band in the region close to Si bandgap is shown at different flux levels.

As can be seen, the efficiency of band-to-band excitation decreases with the wavelength (700-1000 nm range) reflecting the decreasing absorptio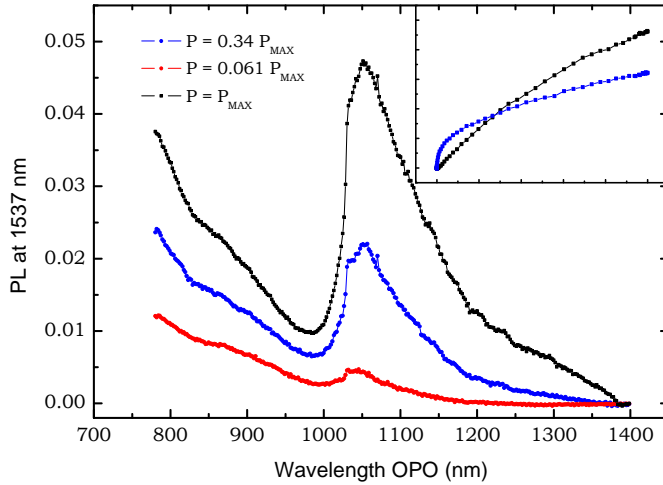n coefficient of Si. At the same time the flux dependence of PL intensity – inset, black curve – can be well described within the model involving electron-hole recombination. At still longer wavelength, however, a resonant feature appears with a maximum around ~1050 nm. This corresponds to a different and thus far unrecognized Er excitation path with a linear dependence on the flux of incoming photons – inset, blue curve. The linear dependence indicates that in this case the excitation process involves transition of a type of carriers to a level in the bandgap. The most striking feature of this

Fig.4: *PLE of the 1.5 µm emission form Si/Si:Er nano-layers for three different flux density levels. The inset compares intensity of the 1.5 µm band as function of photon flux for the band-to-band (black points) and resonant (at 1050 nm, blue points) pumping*

process is that due to the linear character, its efficiency at higher pumping rates exceeds that of the "conventional" exciton-like excitation. Moreover, within the accessible flux range, no indication of saturation has been found. It remains now to be seen whether in carefully engineered nanolayer structures, this process can lead to population inversion, and stimulated emission. This issue will be a major research task of the group of PI.

Relevant papers prepared within the project period
APS journals
1. M. Forcales, T. Gregorkiewicz, M.S. Bresler, O.B. Gusev, I.V. Bradley, and J-P. Wells, *"Microscopic model for non-excitonic mechanism of 1.5 µm photoluminescence of the Er³⁺ ion in crystalline Si"*, Phys. Rev. B **67**, 085303:1-10 (2003).
2. N.Q. Vinh, H. Przybylińska, Z.F. Krasil'nik, and T. Gregorkiewicz, *"Microscopic structure of Er-related optically active center in crystalline Si"*, Phys. Rev. Lett. **90**, 066401:1-4 (2003).
3. M. Forcales, T. Gregorkiewicz, and M.S. Bresler, *"Auger deexcitation of Er³⁺ ions in crystalline Si optically induced by midinfrared illumination"*, Phys. Rev. B **68** 035213:1-7 (2003).
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1. N.Q. Vinh, H. Przybylińska, Z.F. Krasil'nik, and T. Gregorkiewicz, *"Magneto-optical study of Er³⁺-related center in selectively doped Si:Er"*, Physica E **16**, 544-546 (2003).
2. H. Przybylińska, N.Q. Vinh, B.A. Andreev, Z.F. Krasil'nik, and T. Gregorkiewicz, *"Microscopic structure of Er-related optically active centers in Si"*, MRS Symposia Proceedings Vol. **770**, pp. 3-10, edited by Tom Gregorkiewicz, Robert G. Elliman, Philippe M. Fauchet, James A. Hutchby, Materials Research Society, Warrendale, Pennsylvania (2003).

3. B.A. Andreev, Z.F. Krasil'nik, D.I. Kryzhkov, A.N. Yablonskii, V.P Kuznetsov, T. Gregorkie-wicz, M.A.J. Klik, *"Er^{3+} photoluminescence excitation spectra in erbium-doped epitaxial silicon structures",* Physics of Solid State **46**, 97-100 (2004).

5. 2.7 μm EMISSION FROM Er-DOPED Si

The 2.7 μm emission from an Er^{3+} ion corresponds to the $^4I_{11/2} \to \, ^4I_{13/2}$ radiative transition. Therefore, in order to realize it sufficient population of the second excited state $^4I_{11/2}$ has to be obtained. This is best realized by direct optical pumping of the $^4I_{15/2} \to \, ^4I_{11/2}$ transition at 980 nm, as commonly done in optical amplifiers and lasers based on Er-doped insulators. Similarly, this excitation should be possible for Er-doped large-bandgap semiconductors – see Sec. 1 of this report. Once the $^4I_{11/2}$ state has been populated, radiative recombination might proceed, provided that alternative channels of nonradiative recombination are not available – see Sec.6.

This simple excitation scheme cannot be used in Si whose bandgap energy is lower than the separation between the $^4I_{11/2}$ and the $^4I_{15/2}$ states. Therefore simultaneously meeting the two necessary conditions of the 2.7 μm – a sufficiently high concentration of the $^4I_{11/2}$ excited state and suppression of its nonradiative relaxation – represents a major challenge. Nevertheless, in opinion of PI there are no fundamental reasons that would preclude realization of the 2.7 μm emission from Si:Er. In this case the $^4I_{11/2}$ excited state has to be reached in a two-step process, in which the Er^{3+} ion is first brought to the lowest excited state $^4I_{13/2}$. From here the excitation process has to proceed further, e.g., by upconversion or by excited state absorption. Therefore, a sufficiently high concentration of Er ions in the first excited state is required. This is most conveniently achieved by indirect excitation via the Si host, and efficiency of this process is known to be radically improved by co-doping with oxygen. However upon presence of interstitial O in Si, a strong local phonon band appears at 9 μm: this can then be used to promote efficient multiphonon transition between the second and the first excited levels of an Er^{3+} ion, in a similar manner as in oxygen in SiO$_2$:Er. (This according to a general rule that nonradiative multiphonon processes can successfully compete with radiative transitions with energies not larger than ~5 phonons: $\Delta E \lesssim 5E_{phn}$). Such nonradiative quenching should not take place for oxygen-lean Si, as Si phonons have considerably lower energies.

Since on the one hand the precise role of oxygen in promotion of optical activity of Er in Si is not understood, and on the other hand from the existing reports it appears that high concentrations of Er in the first excited state can be obtained by impact excitation with hot electrons, we have investigated a possibility to achieve the 2.7 μm emission by excited state absorption in the mid-infrared region. The results of this study, which will appear shortly in Phys. Rev. B, show that such an excitation scheme is plausible, and should yield appreciable concentration of the $^4I_{11/2}$ excited state. Future experiments will tell whether the theoretically developed model can be realized in practice.

Relevant papers prepared within the project period

APS journals
1. A.S. Moskalenko. I.N. Yassievich, M. Forcales, M.A.J. Klik, and T. Gregorkiewicz, *"Terahertz-assisted excitation of the 1.5 μm photoluminescence of Er in crystalline Si",* to appear Phys. Rev. B (2004).

6. DETAILED RECOMBINATION TRACKING OF Er^{3+} IONS IN A LARGE BANGAP HOST: Photoluminescence of Cs$_2$NaYF$_6$:Er

For various reasons, the hydrothermally grown Er^{3+}-doped Cs$_2$NaYF$_6$ crystals form an interesting model system for studying radiative/non-radiative transition rates and the effects of interactions between Er^{3+} ions in wide bandgap solids. Firstly, due to a very wide bandgap (~ 11 eV) of the host, the Er^{3+} ions can only be resonantly excited and bandgap excitation can be excluded. Secondly, Er^{3+} ions can be incorporated at only one type of well-spaced crystal sites (Y^{3+} site). Further, the symmetry of the crystal field on the Er site is cubic (O$_h$) which implies that, only magnetic dipole zero phonon lines are symmetry allowed. Consequently, the lifetimes of excited states may become very long. Finally, the phonon spectrum (and especially cut-off frequency) of Cs$_2$NaYF$_6$ is comparable to that of nitrides. Therefore conclusions about radiative and non-radiative transition rates may be also valid for Er^{3+} ions embedded in these types of hosts.

The study has mainly been concentrated on the 1.5 μm luminescence, which is most efficiently excited at 515 nm, corresponding to the ^{4}I$_{15/2} \rightarrow$ ^{2}H$_{11/2}$ transition. Upon this excitation, additional luminescence due to the ^{4}I$_{11/2} \rightarrow$ ^{4}I$_{15/2}$, ^{4}F$_{9/2} \rightarrow$ ^{4}I$_{15/2}$ and ^{4}S$_{3/2} \rightarrow$ ^{4}I$_{13/2}$ transitions is also observed. Other transitions are either non-radiative or occur in the mid-IR range, inaccessible for the detectors used in the study.
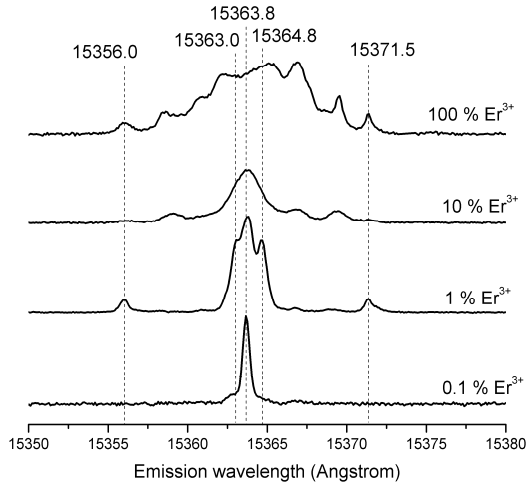

Fig.5: *Low-temperature (4.2 K) high-resolution PL spectra of the 1.5 μm band in Cs$_2$NaYF$_6$:Er^{3+} as a function of Er^{3+} concentration, upon resonant excitation to the ^{2}H$_{11/2}$ state. (514.5 nm, Ar$^+$ laser). The wavelengths (in Å) of the most prominent transitions in the 0.1 % and 1 % doped crystals are indicated (dashed lines)*

As illustrated in Fig.5, high-resolution luminescence spectra of the ^{4}I$_{13/2} \rightarrow$ ^{4}I$_{15/2}$ transition at 4.2 K exhibit an increasingly complicated structure, when increasing the Er^{3+} concentration. Additional transitions observed in the 1 % doped crystal – two doublets of lines symmetrically spaced around the transition occurring in the 0.1 % doped crystal – may reasonably be assumed to be related with Er^{3+} pairs whose formation apparently leads to a symmetrical splitting of the observed spectral line. In the 10 % doped crystal, considerable concentrations of higher Er^{3+} aggregates (triples, quadruples, etc.) may also be expected, whereas in the 100 % doped crystal the number of Er^{3+} ions with which each Er^{3+} ion interacts is only limited by the interaction range.

Time-resolved spectra have been recorded for the ^{4}I$_{13/2} \rightarrow$ ^{4}I$_{15/2}$ luminescence of the 0.1 % and 1 % doped crystals. The results give direct information on the lifetime of the first and the second excited states, which are listed in Table 1. For each luminescence peak, excitation to the second or higher excited states leads to a luminescence rise time of several milliseconds and an even longer decay time, which are essentially independent of the excitation wavelength. Only when direct excitation to the ^{4}I$_{13/2}$ level occurs, the rise time is reduced to the detector response time (~ 100 μs).

Table 1: *Excited state lifetimes for Er^{3+} related centers in Cs_2NaYF_6.*

Emission wavelength (Å)	Lifetime of $^4I_{11/2}$ / $^4I_{13/2}$ states (ms)				
	15356.0	15363.0	15363.8	15364.8	15371.5
$C(Er^{3+})$ = 0.1 %			21 / 51		
$C(Er^{3+})$ = 1 %	14 / 39	20 / 112	21 / 100	22 / 115	14 / 39

These results directly prove that only transitions from the second $^4I_{11/2}$ and the first $^4I_{13/2}$ excited states to the ground state $^4I_{15/2}$ precede radiatively, while all the other relaxations of the 4f-electron shell are predominantly governed by nonradiative recombination. In particular, the lifetime measurements indicate that the $^4I_{9/2} \rightarrow {}^4I_{11/2}$ transition (~ 270 meV) is non-radiative, whereas the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ (~2.7 µm = 460 meV) is radiative and may be detected in the mid-IR range. In this respect it is interesting to note that the maximum lattice phonon energy for this material is estimated in the 450-500 cm^{-1} range (55-63 meV), suggesting that even at 4.2 K non-radiative transitions involving up to 4-5 phonons may occur. In view of the afore mentioned basic similarities between the host used in this experiment with GaN, we therefore conclude that radiative $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition could possibly be realized also for Er in GaN, provided that an Er-related optical center of sufficiently high symmetry could be realized.

7. CONCLUSIONS

In addition to the immediate experimental results of the individual research tasks summarized in relevant sections, also a more general conclusion on Er doping emerges from the project. It is clear that the potential of this possibly most investigated optical dopant is far from exhausted. It seems to offer still new possibilities in different hosts:

- For GaN, the current control and understanding of its optical activity is clearly in the initial stadium. At this moment, it is clear that different centers can be created, and that optical transitions between various states may be realized. The excitation mechanisms and energy migration between individual centers and between Er and the host need to be worked out.

- The issue of sensitization of SiO_2:Er by Si nanocrystals appears to be solved: unless some kind of micro-organization can be introduced into this nonhomo-genous medium, e.g., in a form of an ordered "lattice" of Er- Si-nc pairs, this system is of little practical importance. That in spite of all the publicity that it has recently received

- The multinanolayer structures open a totally new, and unexpected, range of possibilities. These were only briefly addressed in this project but are potentially extremely interesting. The most important here are: preferential generation of a single type of optical center, high percentage of Er atoms participating in emission, new non-saturating excitation mechanism indicating suppression of Auger quenching.

- The possibilities of Er-doped crystalline silicon seem to be exhausted. Yet also here deeper understanding of energy transfer processes, as gained from the nanolayer structures, can result in new opportunities.

It is clear that optical doping of semiconducting matrices is a very rich field with many new phenomena and almost unlimited possibilities in applications for development of efficient light-emitting solid-state sources.